Development of a new Polymeric Ionic Liquid stationary phase for use in High-Temperature Gas Chromatography

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INTRODUCTION

Ionic liquids (ILs) are a class of organic salts exhibiting relatively low melting points (generally below 100 ° C) that are attracting the interest of both academia and industry for their unique features. Many ILs have high inertness, negligible vapour pressure, remarkable solvating properties for both organic and inorganic materials, and high tuneability [1]. Allowing them to be synthesized to depict specific optimised chemical and physical properties. Specifically, they feature high thermal stabilities, offering promise for novel application in gas chromatography separations. In fact, the analysis of polar compounds in Gas Chromatography (GC), is nowadays still rather constrained in terms of thermal stability of available polar stationary phases (e.g. PEG). To improve upon this, stationary phases consisting of ionic liquids (ILs) are being developed, as these have both a high thermal stability and show dual nature characteristics [1], allowing them to be used for the separation of both apolar and polar analytes. Moreover, it has been observed that further improvement of thermal stability can be achieved by means of polymerization to obtain a polymerized ionic liquid (PIL) stationary phase [2]. Therefore, a new PIL stationary phase, poly(3-(2-methylbutyl)-1-vinyl-1H-imidazol-3-ium (poly([ViC$_5$Im$^+$][NTf$_2^-$]), was synthesized through free radical polymerization and the characteristics of this stationary phase such as thermal stability and applicability in both GC-FID and GCxGC-FID were investigated. [2]

EXPERIMENTAL

Synthesis

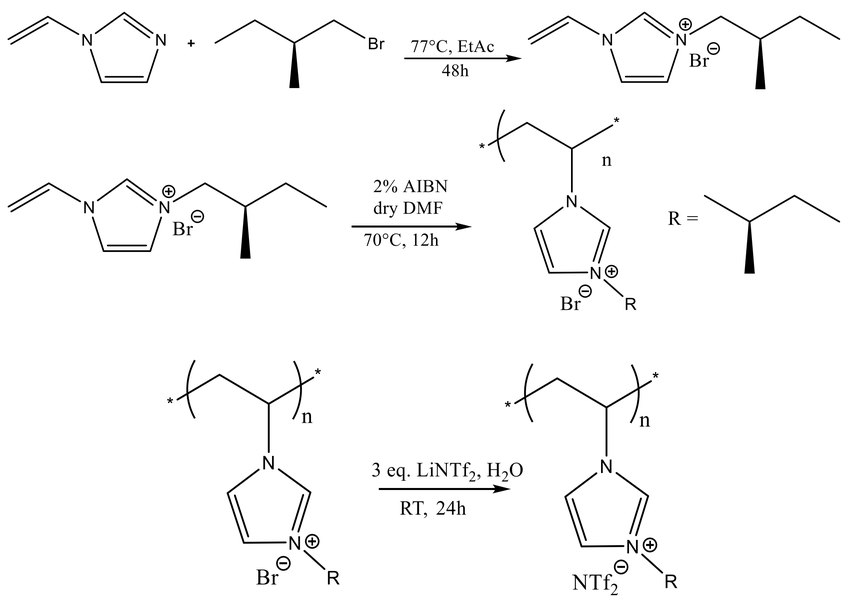


Figure 1. Synthesis of the chain-growth monomer, [ViC$_5$Im$^+$][Br$^-$], followed by free radical polymerization to obtain poly([ViC$_5$Im$^+$][Br$^-$]) and subsequent ion exchange which yields poly([ViC$_5$Im$^+$][NTf$_2^-$]).

Initial measurements of the thermal stability of the poly([ViC$_5$Im$^+$][NTf$_2^-$]) were performed by means of TGA (Figure 3), after which the polymer was coated onto capillary columns (i.d. 0.25mm) by means of the static coating method (Figure 2) to obtain a thickness of film of ~0.35µm. Therefor, a solution of the polymer was prepared in acetone with a concentration of 4mg/ml.

Analytical applications

Column dim.	30m x 0.25mm x 0.35µm
Stationary phase	poly([ViC$_5$Im$^+$][NTf$_2^-$])
Flow rate	1.2mL/min
Temp. Gradient	40 to 200° C (@2.5° C/min)

Table 1. Experimental parameters of the GC-FID measurement of a sample containing 8 polar compounds.

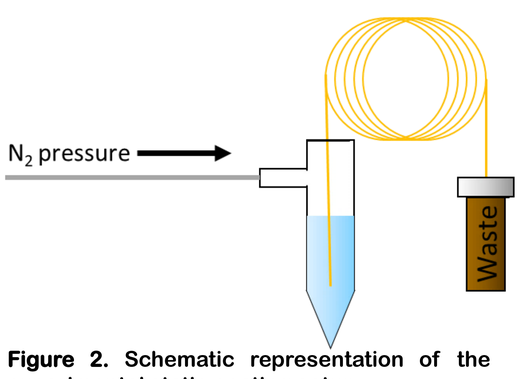


Figure 2. Schematic representation of the experimental static coating setup.

Column (1st dimension)	30m x 0.25mm x 0.25µm
Stationary phase (1st dimension)	PDMS
Flow rate (1st dimension)	0.6mL/min
Column (2nd dimension)	2m x 0.25mm x 0.35µm
Stationary phase (2nd dimension)	poly([ViC5Im+][NTf2-])
Flow rate (2nd dimension)	30mL/min
Temp. Gradient	50 to 225° C (@° 5C/min)
Modulation	Flow-modulation
Modulation time	2.3s (1.5s sampling)

Table 2. Experimental parameters of the GCxGC-FID measurement.

RESULTS & DISCUSSION

Thermal Stability Measurements

As can be observed in the thermogram (Figure 3), an initial weight loss was detected at around 100° C for poly([ViC$_5$Im$^+$][Br$^-$]), which is related to the reported hygroscopic nature of this polymer. By exchanging the bromine anion with bis(trifluoromethane)sulfonimide, an increase in stability of around 50° C is detected. From the bleed measurements (Figure 4), the Maximum operational temperature (MaOT) of the poly([ViC$_5$Im$^+$][NTf$_2^-$] stationary phase was determined to be 250° C.

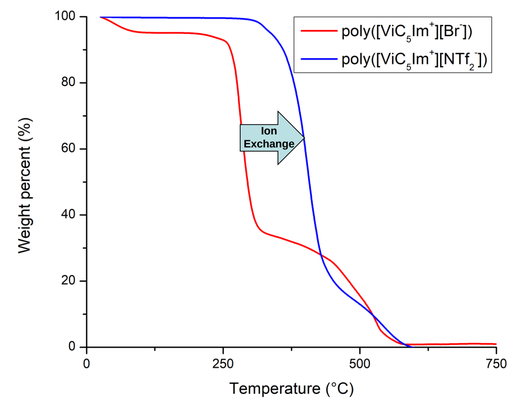


Figure 3. Thermal gravimetric analysis for the poly([ViC5Im+][Br-]) and poly([ViC5Im+][NTf2-]) stationary phases. Temperature program: 25° C – 800° C at a rate of 10° C/min under air flow.

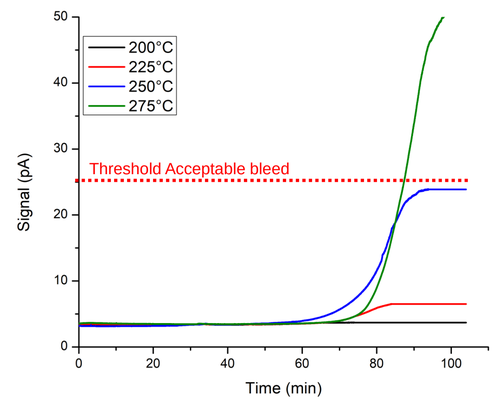


Figure 4. Bleeding profiles of a prepared poly([ViC5Im+][NTf2-]) column (5m x 0.25mm x 0.35µm) using a gradient temperature program starting at 40° C with a heating rate of 10° C/min. Upon reaching the maximum temperature, it was kept constant for an additional 10min.

Separation Characteristics

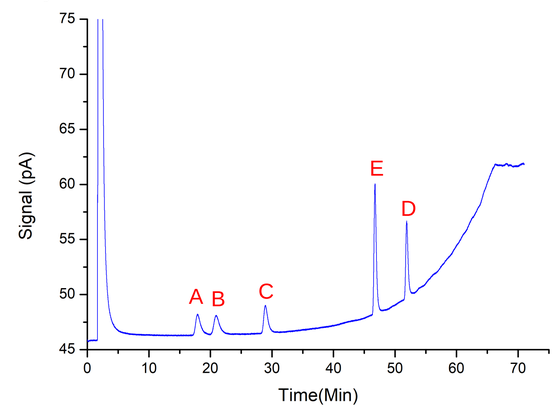


Figure 5: GC-FID Analysis of a sample containing 100ppm of benzaldehyde (A), methylsalycylate (B), 3-nitrotoluene (C), ɣ-nonanoic lactone (D), and benzyl benzoate (E). Experimental details in Table 1.

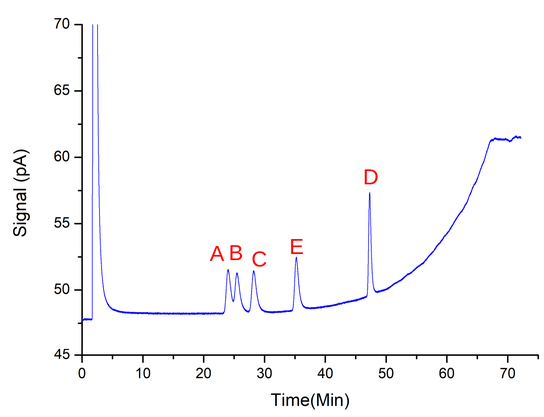
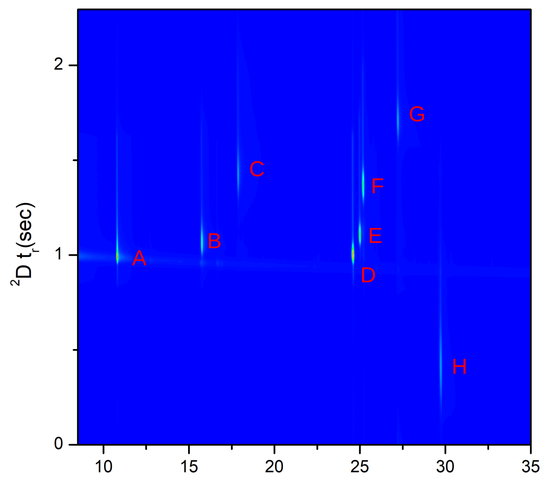


Figure 6: GC-FID Analysis of a sample containing 100ppm of acetophenone (A), propiophenone (B), butyrophenone (C), benzophenone (D), hexanophenone (E) . Experimental details in Table 1.

Satisfying separation and acceptable peak symmetry were obtained for both 1D measurements of polar compounds (Figures 5 and 6) on a column with the poly([ViC$_5$Im$^+$][NTf$_2^-$]) stationary phase (30m x 0.25mm x 0.35µm).



Even at mobile phase velocities well above the optimal velocity, retention and separation was achieved in the second dimension.
This can be observed in Figure 7, where compounds D, E and F would have been poorly resolved when measured in 1D. However, these compounds are well separated on the second dimension.

Figure 7. Analysis of a sample containing 8 compounds at a concentration of 100ppm: toluene (A), anisole (B), aniline (C), butylphenyl ether (D), methylsalycylate (E), 3-nitrotoluene (F), cinnamaldehyde (G), and ɣ-nonanoic lactone (H). Experimental details in Table 2.

CONCLUSION

- Workable thermal stability of the poly[ViC$_5$Im$^+$][NTf$_2^-$] stationary phase (MaOT of 250° C), comparable to the average stability of conventional polar stationary phases.
- Adequate separation of test mixture containing polar compounds was achieved.
- Adequate separation is achieved, even when applying the poly[ViC$_5$Im$^+$][NTf$_2^-$] stationary phase as 2nd dimension in GCxGC-FID. Despite the applied mobile phase velocities vastly exceeding the optimal mobile phase velocity.

REFERENCES

[1] D.W. Armstrong, L. He, Y.S. Liu, Anal. Chem. 1999, 71, 17, 3873-3876.
[2] K. Roeleveld, F. David, F. Lynen, J. Chromatogr. A 2016, 1451, 135-144